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(54) Organic electroluminescence element.

(57) An organic EL element comprises a cathode (1), an EL layer (3) of organic compound, a first hole transport layer (4) of organic compound, a second hole transport layer (4a) of organic compound and an anode (2) which are laminated in sequence, wherein the second hole transport layer (4a) is made of a substance represented by the following chemical formula 1:

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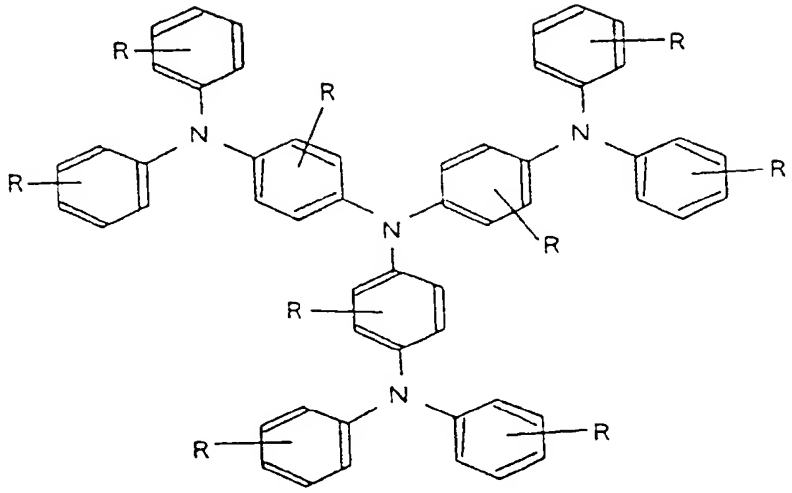
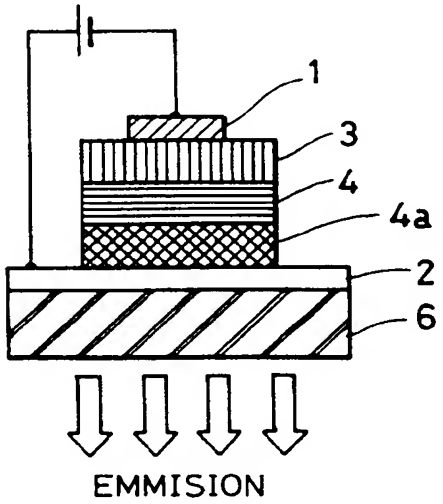
(Chemical formula 1)



where R each independently represents a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, a primary, secondary or tertiary amino group, or an aryl group of from 6 to 15 carbon atoms. This organic EL element prevents a leakage current and emits light stably for a long time.

FIG.3



The present invention relates to an electroluminescence (EL) element having an EL layer made of an emitting substance, which utilizes electroluminescence phenomenon that the emitting substance emits light by applying an electric current to the EL layer. More particularly, it is concerned with an organic electroluminescence element (organic EL element) in which the EL layer is made of an organic emitting substance.

As prior art organic EL elements, there have been known an element of two-layer structure having two layers of organic compounds as shown in Fig. 1, in which an organic fluorescent thin film 3 (hereinafter referred as "EL layer") and an organic hole transport layer 4 are laminated with each other and are arranged between a metal cathode 1 and a transparent anode 2. There have been also known an element of three-layer structure having three layers of organic compounds as shown in Fig. 2, in which an organic electron transport layer 5, an EL layer and an organic hole transport layer 4 are laminated in sequence and are sandwiched as a whole between a metal cathode 1 and a transparent anode 2. The hole transport layer 4 facilitates the infusion of the holes from the anode and blocks electrons. The electron transport layer 5 facilitates the infusion of electrons from the cathode.

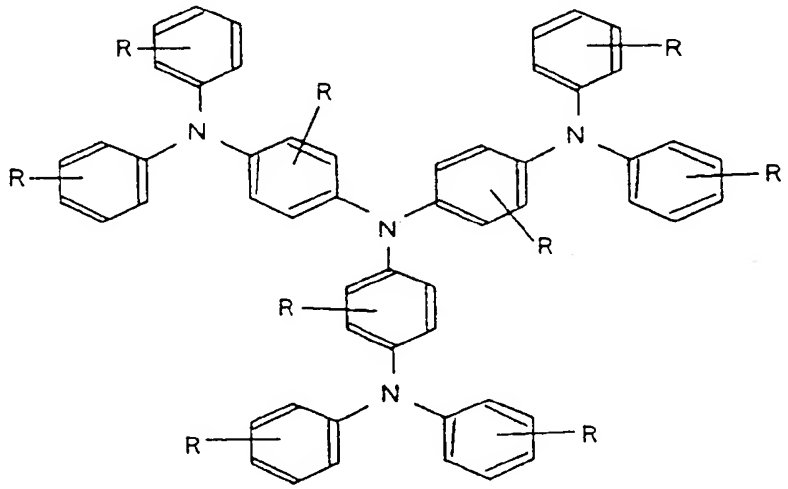
In these organic EL elements, a glass substrate 6 is furnished outside the transparent anode 2. The recombination of electrons infused from the metal cathode 1 and the holes infused from the transparent anode 2 to the EL layer 3 generates excitons. The excitons emit light when they are deactivated through radiation. This light radiates toward outside through the transparent anode 2 and the glass substrate 6 (See Japanese Patent Patents Laid-open Nos.59-194393 and 63-295695).

The conventional organic EL elements constructed as indicated above generally emit light even at a low voltage. However, when the EL element formed with a simple matrix structure of electrode strips is continuously driven by a DC voltage, a leakage current occurs in a cross portion of the electrode strips. As a result, the portion not to emit light i.e. the periphery of the cross portion may emit light, and/or such an EL element easily becomes destructible. Further, there are strong demands on an organic EL element emitting light at a high luminance in the industrial market.

An object of the present invention is to provide an organic EL element, which can prevent the leakage current and stably emit light for a long time and at a high luminance.

The organic EL element according to the present invention comprises a cathode, an EL layer of organic compound, a first hole transport layer of organic compound, a second hole transport layer of organic compound and an anode which are laminated in sequence, wherein the second hole transport layer is made of a substance represented by the following chemical formula 1:

(Chemical formula 1)



where R each independently represents a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, a primary, secondary or tertiary amino group, or an aryl group of from 6 to 15 carbon atoms.

Fig. 1 is a schematic diagram showing an organic EL element with a two-layer structure;

Fig. 2 is a schematic diagram showing an organic EL element with a three-layer structure;

Fig. 3 is a schematic diagram showing an organic EL element with a three-layer structure according to the present invention; and

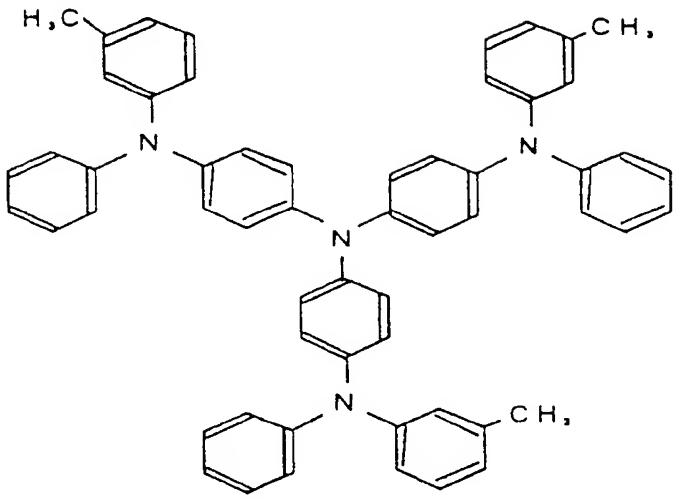
Fig. 4 is a schematic diagram showing an organic EL element with a 4-layer structure according to the present invention.

The embodiments according to the present invention will be described in more detail with reference to the drawings.

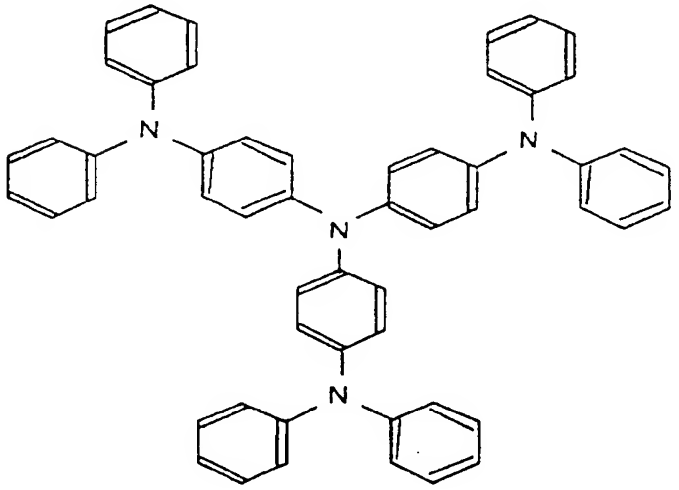
As shown in Fig. 3, a first embodiment of organic EL element according to the present invention comprises an EL layer 3, a first hole transport layer 4 and a second hole transport layer 4a which are laminated and formed as thin films between a pair of metal cathode 1 and transparent anode 2. A second embodiment of organic EL element according to the present invention comprises an electron transport layer 4, an EL layer 3, a first hole transport layer 4 and a second hole transport layer 4a which are arranged between a pair of metal cathode 1 and a transparent anode 2 as shown in Fig. 4. In any of these cases, it will suffice if either the electrode 1 or 2 is transparent. The cathode 1 is formed of a metal with a lower work function such as aluminum, magnesium, indium, silver or alloy of these metals in the thickness range of from about 100 to 5000 Å . The transparent anode 2 is formed of an electroconductive material with a higher work function such as indium-tin oxide (ITO) in the thickness range of from about 1000 to 3000 Å . The transparent anode 2 may be formed of gold with the thickness of from about 800 to 1500 Å . The electrode of gold thin film is semitransparent.

The second hole transport layer 4a is made of the electroluminescent compound represented by the chemical formula 1 such as 4, 4', 4" -tris[N-(3-methylphenyl)-N-phenylamino] triphenylamine (hereinafter referred as "MTDATA") and 4, 4', 4" -tris(N,N-diphenylamino) triphenylamine ("TDATA") respectively denoted by the following formulas 2 and 3:

(Chemical formula 2)



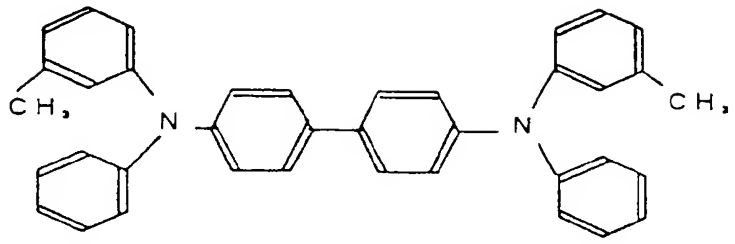
(Chemical formula 3)



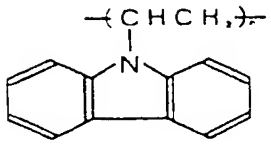
Both MTDATA and TDATA have the melting points of about 203° C or more and the glass transition points of about 75° C, each showing a high heat-resistant property. Also, each of MTDATA and TDATA has a twisted molecular structure and three dimensional frameworks. Thus, these triphenylamine derivatives are easily crystallized and have excellent shielding properties against another substance. Even when a thin film made of one of such triphenylamine derivatives is left at the temperature lower than room temperature for several months, it is not crystallized. Therefore the triphenylamine derivative film maintains its excellent thin film forming property. Further, MTDATA and TDATA have high electric conductivities in the order of 10^{-10} sec/cm. MTDATA and TDATA can be used as the materials desirable for forming EL layer 3.

Next, it is preferable that the first hole transport layer is made of N, N' -diphenyl-N-N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (hereinafter referred as "TPD") represented by the following chemical formula 4. Further, the compounds known as CTM (carrier transporting materials) represented by the following chemical formulas 5 to 15 are suitably used alone or as mixture for the first hole transport layer.

(Chemical formula 4)

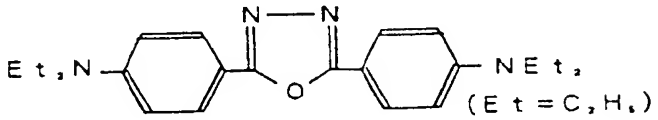


(Chemical formula 5)

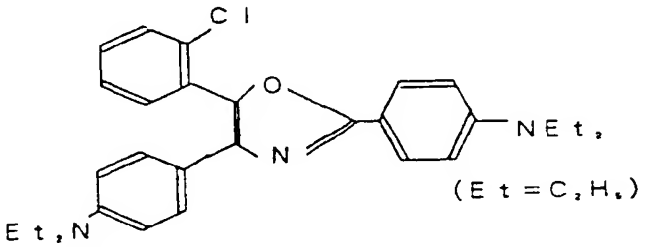


(n represents an integer.)

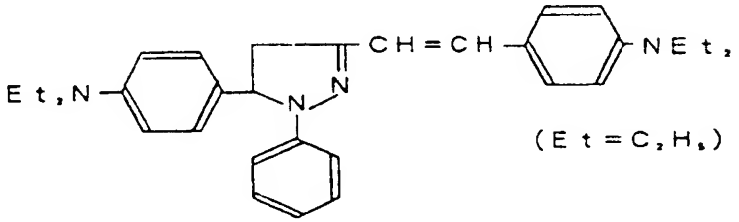
(Chemical formula 6)



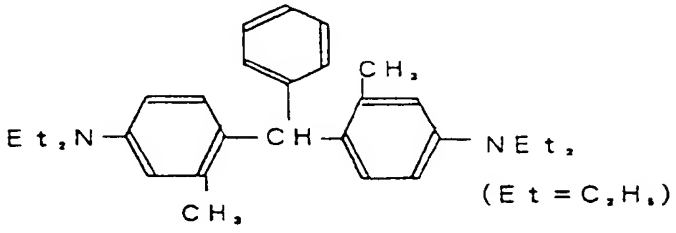
(Chemical formula 7)



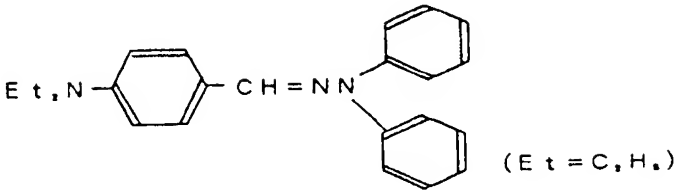
(Chemical formula 8)



(Chemical formula 9)

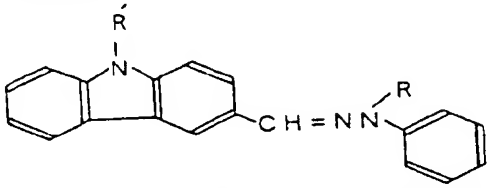


(Chemical formula 10)



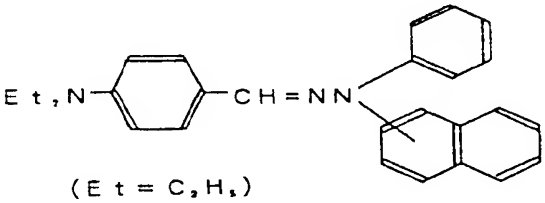
(Et = C_2H_5)

(Chemical formula 11)



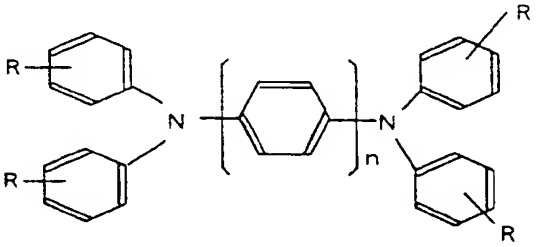
(R and R' represent an alkyl group.)

(Chemical formula 12)



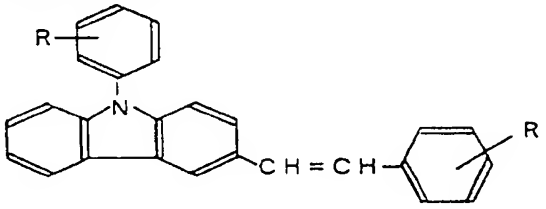
(Et = C_2H_5)

(Chemical formula 13)



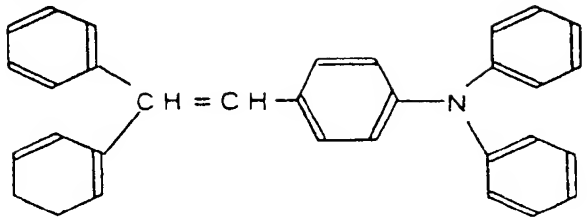
(R represents an alkyl group, and n is an integer.)

(Chemical formula 14)



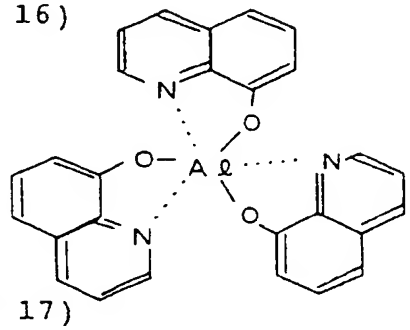
(R represents an alkyl group.)

(Chemical formula 15)

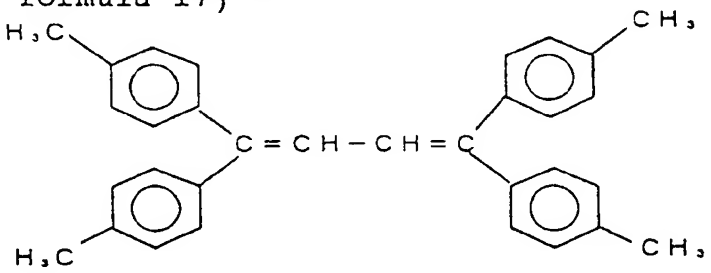


The EL layer 3 of the organic EL element comprises the organic fluorescent compound such as Aluminum oxine chelate (hereinafter referred as "Al_{q3}) and tetraphenylbutadiene (TPB) derivative respectively represented by the following chemical formulas 16 and 17, which may include another fluorescent compound as a guest material.

(Chemical formula 16)

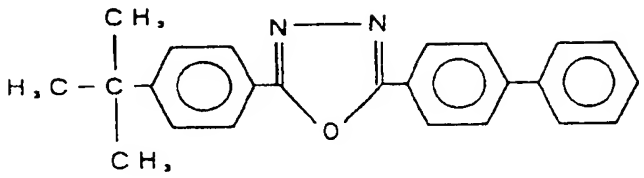


(Chemical formula 17)

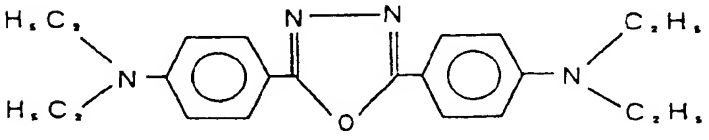


The electron transport layer 5 of organic EL element is preferably made of Bu-PBD [2-(4'-tert-butylphenyl)-5-(biphenyl)-1,3,4-oxadiazole] represented by the following chemical formula 18. Examples of suitable organic compounds which may be employed as the electron transport layer 5 are represented by the following chemical formulas 19 to 28.

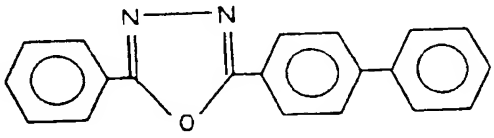
(Chemical formula 18)



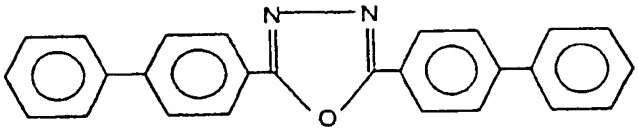
(Chemical formula 19)



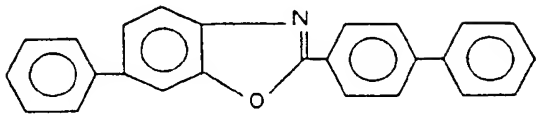
(Chemical formula 20)



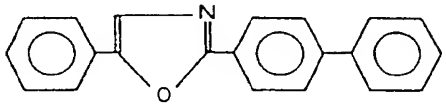
(Chemical formula 21)



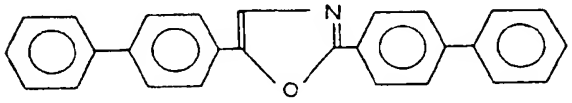
(Chemical formula 22)



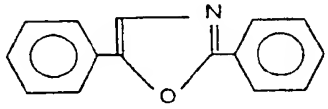
(Chemical formula 23)



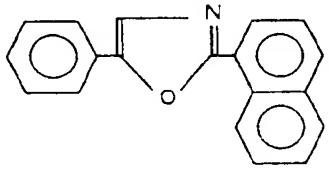
(Chemical formula 24)



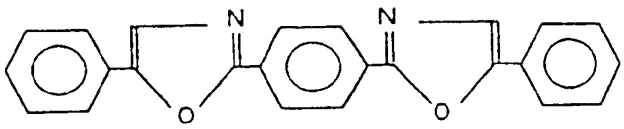
(Chemical formula 25)



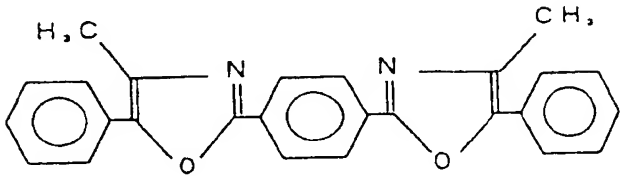
(Chemical formula 26)



(Chemical formula 27)



(Chemical formula 28)



As described above, an organic EL element in accordance with the present invention and comprising the organic EL layer and the first organic hole transport layer laminated with each other and arranged between the cathode and the anode, is characterized in that a second hole transport layer made of triphenylamine derivatives represented by the chemical formula 1 is provided between the first hole transport layer and the anode. The second hole transport layer has a high heat-resistant property. Thus, the second hole transport layer reduces the undesirable influence thereon caused by the heat generated from application of electric current. The second hole transport layer has excellent thin film forming property, it can therefore cover well and deposit even on an irregular surface of the anode. The second hole transport layer then prevents the sharp edge of the anode from coming closer to the cathode. Since, the second hole transport layer has high conductivity, the voltage applied thereon decreases and heating is minimised. In this way, it is possible to improve the durability of the organic EL element which emits light at a high luminance and a high efficiency upon application of a low voltage.

(Example 1)

A well washed glass substrate was prepared, on which an anode of ITO had been formed. MTDATA of chemical formula 2 was heated under vacuum conditions and deposited on the ITO anode with the thickness of 200 Å as the second hole transport layer. Next, TPD of chemical formula 4 was heated under vacuum conditions and deposited on the MTDATA layer with the thickness of 300 Å as the first hole transport layer. Then, Al_{q3} of chemical formula 16 was heated under vacuum conditions and deposited on the TPD layer with the thickness of 500 Å as the EL layer. Next, magnesium and aluminum were vacuum deposited on the EL layer of Al_{q3} with the thickness of 1500 Å under vacuum conditions at the vacuum deposition rate of 10 Å /sec and 1 Å /sec respectively as the metal alloy cathode. In this way, the EL element was manufactured.

When the resultant EL element was operated with the application of DC voltage at the constant current density of 10 mA/cm^2 for 600 hours, then its output luminance was attenuated from the initial 400 cd/m^2 to the elapsed 225 cd/m^2, while the increase of the applied voltage was only 2 V during this time period. This shows a high driving stability of the EL element.

(Comparative example 1)

As an EL element was produced by the same procedure as in the above Example 1, excepting that the second hole transport layer made of MTDATA was not formed.

When this EL element was operated at the constant current density of 10 mA/cm^2 for about 250 hours, a leakage current occurred at points other than the light-emitting points. This El element therefore did not emit light, showing an instability as an EL element.

(Example 2)

Instead of EL layer of Al_{q3} in the Example 1, an EL element was assembled by the same procedure as in the Example 1 while using EL layer of TPB derivative represented by chemical formula 17.

When this EL element was operated at the constant current density of 50 mA/cm^2 for about 175 hours, the initial output luminance of 80 cd/m^2 was attenuated to the elapsed output luminance of 10 cd/m^2, while the increase of the applied voltage was only 2 V during this time period. This shows a high driving stability of the EL element.

(Comparative example 2)

An EL element was assembled by the same procedure as in the Example 2, except that the second hole transport layer made of MTDATA of the Example 2 was not formed.

When this EL element was operated at the constant current density of 27 mA/cm^2 for about 10 hours, the luminance was attenuated from 80 cd/m^2 to 1 cd/m^2, and the element was destroyed.

(Comparative example 3)

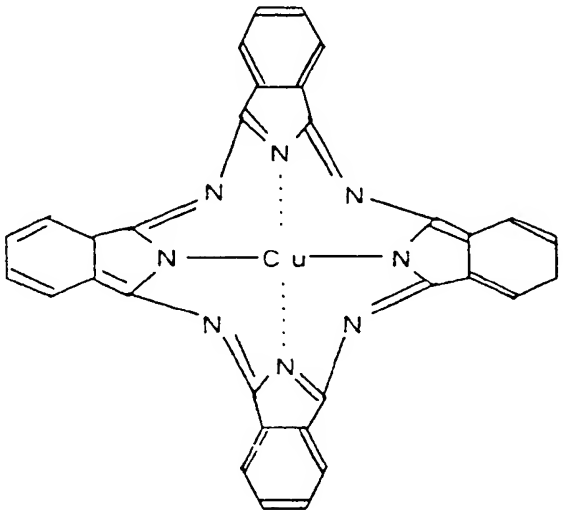
An EL element was assembled by the same procedure as in the Example 2, except that Bu-PBD represented by the above chemical formula 18 was vacuum-deposited and laminated with the thickness of 300 Å as the electron transport layer.

When this EL element was continuously drive, the hue of emitted light was changed within a short time and it was destroyed. When such an EL element was operated at the constant current density of 5 mA/cm^2, it emitted light at 80 cd/m^2, but it was destroyed in 3 hours while the hue was changed from blue to white.

(Comparative example 4)

Instead of the second hole transport layer made of MTDATA of the Example 2, an EL element was assembled by the same procedure as in the Example 2, except that the second hole transport layer made of Cu-Ph represented by the following chemical formula 29 was used.

(Chemical formula 29)



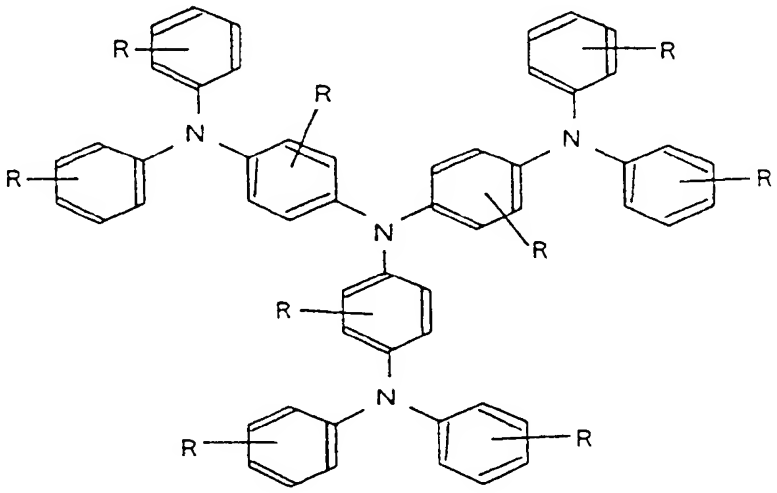
When this EL element was operated at the constant current density of 27 mA/cm^2 for about 19 hours, its luminance was attenuated from 80 cd/m^2 to 0 cd/m^2.

Claims

1. An organic electroluminescence element, comprising a cathode (1), an EL layer (3) of organic

compound, a first hole transport layer (4) of organic compound, a second hole transport layer (4a) of organic compound and an anode (2) which are laminated in sequence, characterised in that the second hole transport layer (4a) of a substance represented by the following chemical formula 1:

(Chemical formula 1)



where R each independently represents a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, a primary, secondary or tertiary amino group, or an aryl group of from 6 to 15 carbon atoms.

2. An organic electroluminescence element according to Claim 1, wherein an organic electron transport layer (5) is provided between said cathode and said fluorescent layer.

FIG.1

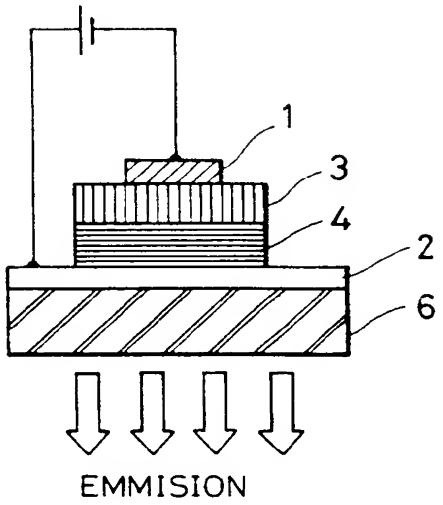


FIG.2

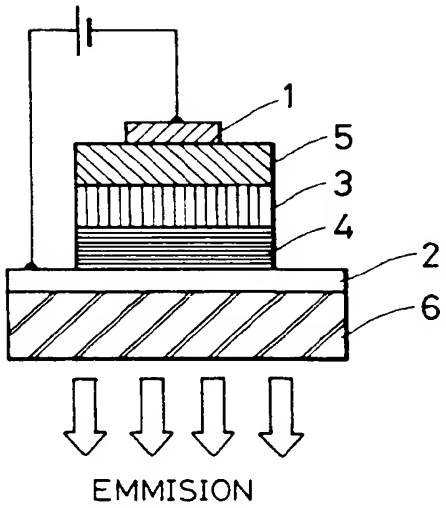


FIG.3

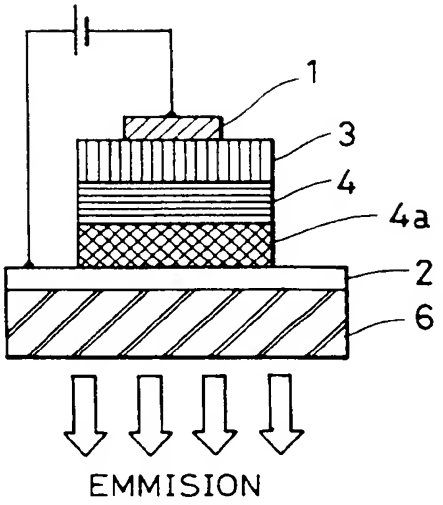
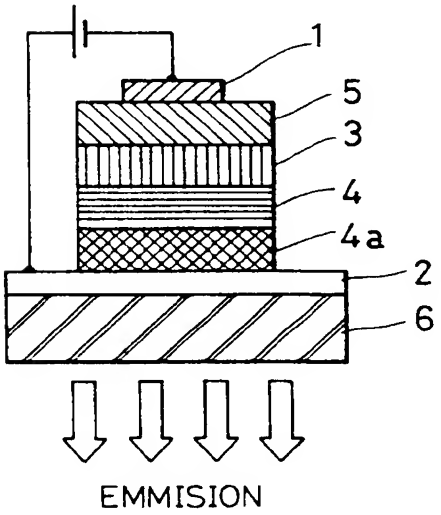


FIG.4



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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 0094

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 549 (C-662)7 December 1989 & JP-A-1 224 353 (BANDO CHEM) * abstract *	1	H05B33/14 H01B1/12 C07C211/54
Y	PATENT ABSTRACTS OF JAPAN vol. 15, no. 101 (M-1091)11 March 1991 & JP-A-3 000 291 (RICOH) 7 January 1991 * abstract *	1	
Y	CHEMISTRY LETTERS vol. 89, no. 2, 1989, JAPAN pages 1145 - 1148; Y.SHIROTA &AL: 'starburst molecules...'	1	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 358 (P-916)10 August 1989 & JP-A-1 118 142 (MITA) 10 May 1989 * abstract *		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

H05B
H01B
C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 MAY 1992	DROUOT M.C.

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